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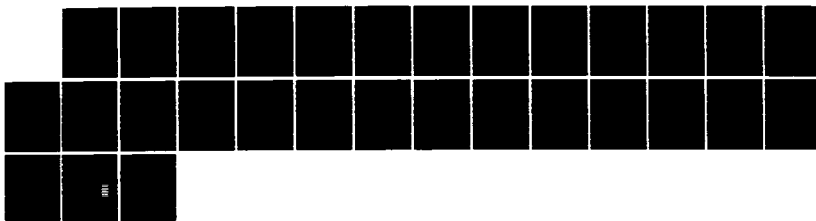
THE ELECTRONIC AND VIBRATIONAL ENERGIES OF THE
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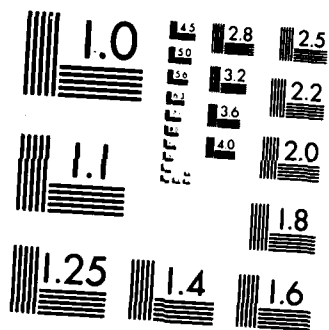
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TECHNICAL REPORT BRL-TR-2733

THE ELECTRONIC AND VIBRATIONAL ENERGIES
OF THE HIGH-SPIN STATES OF He_2
WHICH CORRESPOND ASYMPTOTICALLY TO THE
INTERACTION OF TWO $1s2s^3S$ He ATOMS

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June 1986

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20. Abstract (Cont'd):

Reliable values of the dipole-, quadrupole-, and octupole-polarizabilities of the triplet atom are calculated at the CI level in the course of developing our basis set.

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I. INTRODUCTION

Nearly two decades ago, Klein¹ was the first to compute the potential energy curves for the 1_g^+ , $3_{\Sigma_u}^+$, and $5_{\Sigma_g}^+$ states of He_2 which arise from the interaction of two $1s2s\ 3S$ ($2\ 3S$) atoms using generalized valence bond functions. He was able to obtain a rigorous upper bound on the energy of the $5_{\Sigma_g}^+$ state, since it is the lowest-lying state of its symmetry. The calculation of the curves for the $3_{\Sigma_u}^+$ and $1_{\Sigma_g}^+$ states posed special problems for Klein since these states are unstable with respect to autoionization to some state of He_2^+ and because these doubly excited states lie above a denumerable infinity of neutral molecules of the same symmetries. Klein recognized that he could not apply the Hylleraas-Undheim variation principle to the calculation of their potential curves. Instead he used a stabilization method to approximate them.

About four years later, Garrison, Miller and Scheaffer (GMS)² treated these same three states in connection with their study of Penning and associative ionization of $2\ 3S$ atoms. GMS performed a configuration interaction (CI) calculation in which they extracted an excited root of the CI matrix which corresponded asymptotically to the interaction of a pair of $2\ 3S$ atoms. These computations were insufficiently extensive to provide the framework which would allow Gillen, Petersen, and Olson³ to interpret their own experiments on the ion production resulting from the collisions of $\text{He}\ 1s2s\ 1S$ ($=2\ 1S$) with ground state $\text{He}\ 1s^2\ 1S$ atoms. In a companion paper Saxon, Gillen, and Liu (SGL)⁴ postulated a mechanism for ion production which involved the $1_{\Sigma_g}^+$ state (corresponding to the $2\ 3S + 2\ 3S$ interactions) and selected lower-lying states of the same symmetry by means of a state-averaged multiconfiguration self consistent field procedure. SGL found that the adiabatic $1_{\Sigma_g}^+$ state had an interesting metastable well near 1.5 bohr which was vital in interpreting the scattering results.

We have recently undertaken a study of high spin states of He_2 in connection with our investigations of spin-orbit interactions. In the course of this study we have calculated the adiabatic potential curves for the $3_{\Sigma_u}^+$ and $5_{\Sigma_g}^+$ states corresponding to the interaction of a pair of $2\ 3S$ atoms. In view of the interest in a number of quarters¹⁻⁶ in having available high-quality potential curves to enhance their studies, we report our excited state potential curves now in advance of the completion of other parts of our investigations.

In the following section we discuss the all-important questions of basis set development and method of calculation. Next, we present our calculated potential curves and compare them with the results of previous calculations. Finally, we present our calculated vibrational energy levels.

II. BASIS SET DEVELOPMENT AND METHOD OF CALCULATION

The basis set listed in Table 1 was chosen primarily to describe the $2\ 3S$ atom energy reasonably accurately. This is much easier to accomplish for this singly excited state since the inter-shell correlation energy in the triplet is small relative to the intra-shell correlation energy in the ground state atom. The most diffuse p-, d-, and f-functions in our basis were optimized

to give the best (largest) dipole-, quadrupole-, and octupole-polarizabilities of the 2^3S atom at the full CI level of accuracy. Table 2 shows that we obtain excellent agreement with accurate literature values of the atomic energy^{7 8} and dipole polarizability.^{9 10} We are unaware of published values of either the quadrupole or octupole polarizability for this triplet atom. Nevertheless we are quite confident that our calculated polarizabilities are quite accurate.

Table 1. Slater Basis Set for He

Number	n	l	ζ
1	1	0	5.671
2	2	0	3.28
3	1	0	2.0084
4	2	0	4.91718
5	2	0	1.63438
6	2	0	0.60962
7	2	1	2.7
8	2	1	2.0
9	2	1	1.0
10	3	1	2.2
11	3	1	0.600
12	3	1	4.15
13	3	2	2.2
14	3	2	1.6
15	4	2	0.56
16	4	2	2.82
17	4	3	0.446

Table 2. Atomic Properties for He 2^3S

Energy (Hartree)	
Present SOCI	-2.17521
Numerical MCSCF (Ref. 6)	-2.17522
Exact (Ref. 8)	-2.17523
Dipole Polarizability (au)	
Present	316.64
Victor, et al., (Ref. 9)	316.2
Chung (Ref. 10)	315.63
Quadrupole Polarizability (au)	
Present	2743.3
Octupole Polarizability (au)	
Present	89 551

We calculated atomic polarizabilities by two methods. First we calculated the appropriate field dependent multipole moment $\mu_n(F_n)$, and from it calculated the polarizability

$$\alpha_n = \lim_{F_n \rightarrow 0} \mu_n(F_n)/F_n.$$

We took the limit of a converging sequence of such polarizabilities obtained with successively smaller fields to be the desired polarizability. Here F_n is the 2n-pole electric field of strength F . The second method depends on calculating the energy perturbation due to the applied external field. In this case it is easy to show¹¹ that

$$\alpha_n = \frac{\partial^2 E(F_n)}{\partial F_n^2} \approx \frac{2[E(0) - E(F_n)]}{F_n^2}$$

in the limit of vanishing field strength. The results of the two methods agreed to at least the number of significant figures to which the polarizabilities are reported in Table 2.

The potential energy curve for the $^5\Sigma_g^+$ state was calculated with a basis set lacking the tight functions #12 and #16 listed in Table 1; these functions were optimized for the $1s2s\ ^1S$ atom energy. Thus, the CI for the quintet was based on one ϕ , four δ , nine π , and 15 σ molecular orbitals each of g and u inversion symmetry; that for the $^3\Sigma_u^+$ calculation was based on one ϕ , five δ , eleven π , and 17 σ molecular orbitals each of g and u symmetry. The tight p - and d - atomic orbitals which distinguish the two calculations are of no particular consequence to the calculation of the potential curves of interest here. They will account for a very small amount of atomic correlation energy and essentially no molecular correlation energy. Thus, we consider the calculations of the $^3\Sigma_u^+$ and $^5\Sigma_g^+$ potential curves to be on essentially equal footing insofar as basis set is concerned.

Consider the computation of the $^5\Sigma_g^+$ curve. We use the orbitals from a self-consistent field (SCF) computation for this state as input for a multiconfiguration self-consistent field (MCSCF) calculation in which four electrons were allowed to occupy any of three σ or one π orbitals each of g or u inversion symmetry subject to the constraints imposed by $^5\Sigma_g^+$ molecular symmetry. There were 31 such configuration state functions (CSF). The MCSCF computation was then used as a base for a second order configuration interaction (SOCi) variational calculation wherein all single and double excitations from the 6 σ and 2 π base were allowed, subject to the constraints imposed by $^5\Sigma_g^+$ symmetry. The SOCi calculation comprised 15,220 CSFs. Of course, such a SOCi calculation is not size consistent: the separated atoms are completely correlated while the molecule is not. By comparing the energy of the separated atoms with the energy calculated for the quintet molecule at $R = 50\ a_0$, we estimate a size consistency error to be about $15.1\ \text{cm}^{-1}$.

We performed a test of the basis set superposition error (BSSE) according to the counterpoise technique of Boys and Bernardi.¹² At an internuclear separation $R=7.5\ a_0$, which is essentially the position of the minimum in the $^5\Sigma_g^+$ curve, the BSSE was determined to be only $0.02\ \text{cm}^{-1}$ at the SCF level and $0.3\ \text{cm}^{-1}$ at the SOCi level. We estimate that the BSSE for the $^3\Sigma_u^+$ state would be less than ten times as large at that separation.

Our approach to the calculation of the ${}^3\Sigma_u^+$ state corresponding to the interaction of a pair of $2\,{}^3S$ atoms was somewhat different. Here, we first computed the SCF wavefunction for the lowest-lying ${}^3\Sigma_u^+$ state (commonly called a ${}^3\Sigma_u^+$) which corresponds asymptotically to the $\text{He } 1s2s\,{}^1S + \text{He } 1s2s\,{}^3S$ interaction. We used the resulting molecular orbitals as input for an MCSCF calculation wherein the four electrons were allowed to occupy any combination of two σ_u and two σ_g orbitals subject to the constraints imposed by ${}^3\Sigma_u^+$ symmetry. This results in eight CSFs. The vectors from the lowest lying triplet state calculation were used as input to an MCSCF calculation for the excited ${}^3\Sigma_u^+$ state which corresponds to the interaction of a pair of $2\,{}^3S$ He atoms. (We'll call this the $2,1\,{}^3\Sigma_u^+$ state according to the notation scheme we discuss in the Appendix.) The MCSCF comprised those CSFs which result from allowing the four electrons to occupy two σ_g and two σ_u orbitals subject to the constraints imposed by ${}^3\Sigma_u^+$ symmetry and the additional constraint needed to assure a symmetrical dissociation to a pair of $2\,{}^3S$ atoms. That is, the $1\sigma_g$ and $1\sigma_u$ orbitals correlate asymptotically with the He $1s$ orbital and the $2\sigma_g$ and $2\sigma_u$ orbitals correlate with a He $2s$ orbital appropriate to the He $2\,{}^3S$ atom. This resulted in an MCSCF calculation comprising only four CSFs. Finally, a SOCI computation which allowed all appropriate single and double excitations from this 4 CSF base was performed. The SOCI computation comprised 7248 CSFs: the state of interest was the lowest root of the CI energy matrix despite the fact that there exist a denumerable infinity of ${}^3\Sigma_u^+$ states which lie energetically lower. Those states are excluded from the computation by constraining the number of electrons allowed in the $1s$ ($1\sigma_g$, $1\sigma_u$) orbital space to be two. Asymptotically this occupancy constraint will assure our obtaining the desired lowest lying states from the second ionization manifold of states without our needing to impose further constraints of orthogonality to the infinity of ${}^3\Sigma_u^+$ states which lie within the first ionization manifold. However, at smaller separations, it is not evident that our procedure guarantees no mixing with states from the first ionization manifold. We appeal to perturbation theory arguments to assert that the energy gap between the $2,1\,{}^3\Sigma_u^+$ state and even the highest lying state from the first ionization asymptote (i.e., the $1,\infty\,{}^3\Sigma_u^+$ state) is so large that mixing of these states must be negligible. We know only that the gap is some $198,300\text{ cm}^{-1}$ asymptotically (if we ignore the continua). At smaller separations the magnitude of that gap is unknown, so there we can be less certain of our results for the $2,1\,{}^3\Sigma_u^+$ state.

The potential curves resulting from the SOCI computations described above are listed in Table 3 and are discussed in the following section.

III. DISCUSSION OF RESULTS

Our calculated SOCI potential curves are displayed in Figure 1. There it is evident that the $2,1\,{}^5\Sigma_g^+$ state (the lowest state of ${}^5\Sigma_g^+$ symmetry) has a relatively shallow well with its minimum at a relatively large internuclear separation. This is just the sort of van der Waals well one expects to result from the spin-aligned interaction of two highly polarizable atoms in a way which does not admit of ordinary chemical bonding. As we show in Table 4 our ${}^5\Sigma_g^+$ dissociation energy (D_e) is about three times as large as that obtained in Klein's¹ pioneering calculation and it is about 50% larger than the value obtained by GMS.

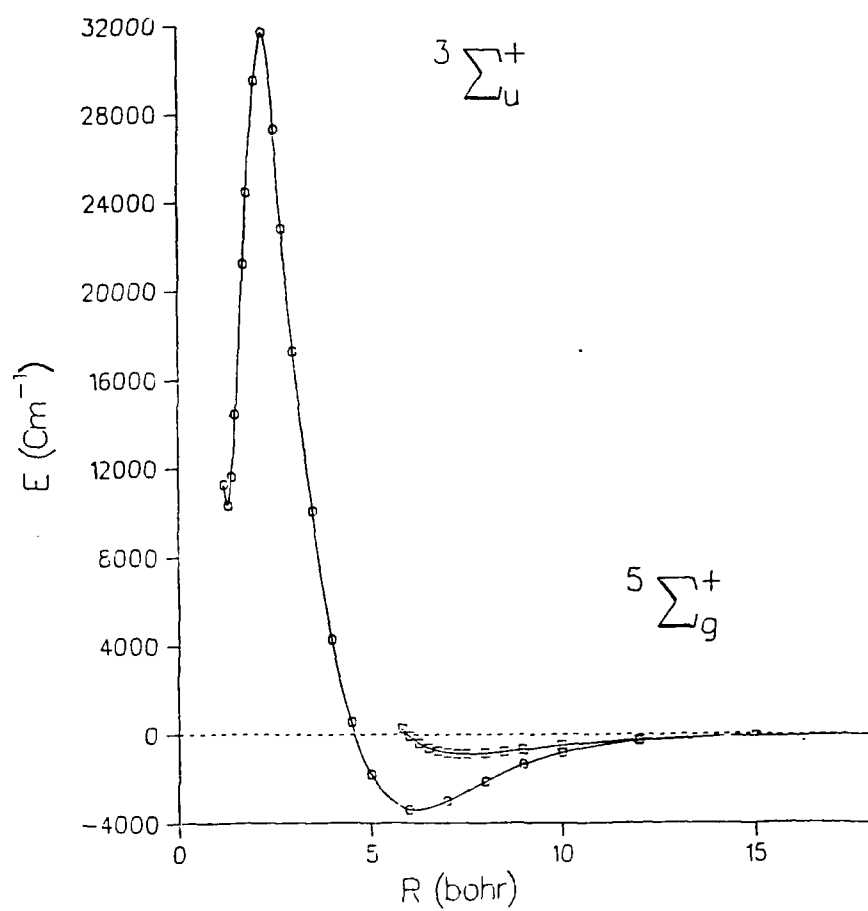


Figure 1. Potential Energy Curves for the $2,1$ $5 \Sigma_g^+$ and $2,1$ $3 \Sigma_u^+$ States of He_2

Since Klein's basis set was reoptimized at each internuclear separation, and his generalized valence bond procedure is so different from ours, we cannot easily make further detailed comparisons with his results.

The GMS calculation, like ours, is a CI of molecular orbitals (MO) comprised of a linear combination of atomic orbitals (LCAO). Thus, it is of interest to compare their results with ours in some detail. The GMS basis set comprised only four s and two p functions while ours comprises six s, five p, three d, and one f functions. Furthermore, certain of the higher angular momentum functions in our basis were optimized specifically to describe the dipole-, quadrupole-, and octupole-polarizability. Since these polarizabilities are very large indeed, as we have shown in Table 2, a computation lacking the functions which are necessary to describe these polarizabilities properly could not possibly describe the van der Waals state at all well. It is, in fact, somewhat suprising that the GMS potential curve is so deep considering the paucity of polarization functions in their basis set.

Table 3. Potential Curve for the $2,1 \ ^5\Sigma_g^+$ and $2,1 \ ^3\Sigma_u^+$ States of He_2

$1 \ ^5\Sigma_g^+$		$a' \ ^3\Sigma_u^+$	
$R \ (a_0)$	$-E \ (E_h)$	$R \ (a_0)$	$-E \ (E_h)$
5.80	4.349093	1.2	4.299090
6.00	4.350644	1.3	4.303397
6.25	4.352079	1.4	4.297519
6.50	4.353070	1.5	4.284677
6.75	4.353722	1.7	4.253823
7.00	4.354119	1.8	4.239145
7.25	4.354319	2.0	4.216234
7.50	4.354379	2.2	4.206290
8.00	4.354221	2.5	4.226173
8.50	4.353864	2.7	4.246539
9.00	4.353435	3.0	4.271716
10.00	4.352603	3.5	4.304495
12.00	4.352469	4.0	4.330934
15.00	4.350754	4.5	4.347748
20.00	4.350470	5.0	4.358615
25.00	4.350429	5.5	4.364097
50.00	4.350347	6.0	4.365936
		7.0	4.364101
		8.0	4.360064
		9.0	4.356583
		10	4.354194
		12	4.351814
		20	4.350470
		100	4.350400

Let us now examine the $2,1 \ ^3\Sigma_u^+$ potential curve in Figure 1. From the asymptotic region down to internuclear separations around three or four bohr the potential curve looks rather ordinary; it has a moderately deep well with

its minimum near 6 bohr. At smaller separations (ca. 2.2 - 2.3 bohr) it undergoes a relatively sharp maximum at about $32,000 \text{ cm}^{-1}$ above the $2^3\text{S} + 2^3\text{S}$ asymptotic energy. At still smaller separations it descends to an even sharper (narrower) minimum around 1.3 bohr which lies over $20,000 \text{ cm}^{-1}$ below the top of the hump but some $11,700 \text{ cm}^{-1}$ above the asymptote, then the curve (presumably) undergoes a steep rise at even smaller separations. None of this interesting short range behavior was noted by GMS whose calculations were limited to separations $R > 4 a_0$. Recall the discussion of our calculation method in the penultimate paragraph of Section II. In view of our uncertainty over the extent of configuration mixing with lower lying states at small internuclear separations, one might suspect that the unusual short-range behavior of the $2,1^3\Sigma_u^+$ state suggests that our calculation is no longer valid in that region. While we are not nearly so confident in our $2,1^3\Sigma_u^+$ curve at small separations as we are at large R , there is at least qualitative support for our result from another quarter.⁴

The potential curve for the $2,1^1\Sigma_g^+$ state (SGL call this their "doubly excited" state) corresponding to the interaction of two 2^3S atoms was obtained by SGL in a "state averaged" MCSCF calculation. Their $2,1^1\Sigma_g^+$ curve shows behavior which is qualitatively similar to that of our corresponding triplet curve: the singlet has a well about 1000 cm^{-1} deep at about $7 a_0$, a high hump at around $2.5 a_0$, and a narrow attractive well with a minimum around $1.5 a_0$ which lies about $12,000 \text{ cm}^{-1}$ above the $2^3\text{S} + 2^3\text{S}$ asymptote. SGL ascribe the unusual shape in the short range of the adiabatic $1^1\Sigma_g^+$ curve to an avoided crossing with the rising repulsive limb of another $1^1\Sigma_g^+$ curve which itself corresponds asymptotically to the interaction of the energetically lowest lying He^+ and He^- ions. The SGL state-averaged MCSCF calculation included what is presumably the highest $1^1\Sigma_g^+$ ($1,\infty^1\Sigma_g^+$) from the singly excited manifold. Thus, their calculation is not subject to the same uncertainty as ours due to the possible mixing of states from the singly and doubly excited manifolds. Since we have not calculated the corresponding $3^3\Sigma_u^+$ ion pair curve, we can neither confirm nor deny that an interpretation similar to that offered by SGL rationalizes the short-range behavior of our triplet curve. It would be interesting to explore this question in more detail especially in the context of $\text{He } 2^3\text{S} + \text{He } 2^3\text{S}$ scattering and the autoionization of the $2,1^3\Sigma_u^+$ state.

Table 4 shows that the GMS calculation yields a $3^3\Sigma_u^+$ potential curve about 1500 cm^{-1} deeper than ours even though their minimum lies somewhat to the right of ours. It seems to us that the GMS calculation, based as it was on a basis set so much smaller than ours may have been subject to a basis set superposition error substantially larger than the 0.3 cm^{-1} which we found. (This would also explain why the GMS $3^3\Sigma_g^+$ curve is suprisingly deep despite the lack in their basis of d and f functions necessary to describe the various multipole polarizabilities of the 2^3S atom.)

In summary, it appears that our potential curves for the two states in question are the best currently available. They appear to be of high enough quality to use them to make quantitative comparison with spectroscopic and scattering experiments.

IV. VIBRATIONAL ENERGY LEVELS

In view of the potential interest of spectroscopists in examining the spectra of highly excited states and in our expectation that our potential curves are reliable, it seems worthwhile for us to calculate the vibrational energy levels for the states in question. The listing in Table 5 shows that the $5\Sigma_g^+$ state has nearly the same number of bound vibrational levels as the $2,1\ 3\Sigma_u^+$ state. In fact, the substantial difference in their equilibrium separations suggests that the gap in the number of (perhaps metastably) bound vibrational levels will narrow somewhat for rather high rotational quantum numbers. This follows, of course, because the rotational quanta for the triplet are about 20% larger than they are for the quintet.

Table 4. Constants for States Corresponding to the $3S + 3S$ Asymptote

<u>Source</u>	<u>R_e (bohr)</u>	<u>D_e (cm⁻¹)</u>
	$5\Sigma_g^+$	
Present	7.509	888.94
GMS (Ref. 2)	7.91	560
Klein (Ref. 1)	~9.	310
	$3\Sigma_u^+$ (Intermediate Range)	
Present	6.150	3428
GMS (Ref. 2)	6.27	4920
Klein (Ref. 1)	~5	3300
	$3\Sigma_u^+$ (Very Short Range)	
Present, min	~1.3	11712
Present, max	~2.2	31629

An examination of the excited atomic energy levels for He suggests that one should look for transitions involving the $2,1\ 5\Sigma_g^+$ state at wavelengths in the neighborhood of 1080 nm to connect with either the $2,1\ 5\Sigma_u^+$ or the $2,1\ 5\Pi_u$ state which themselves correspond asymptotically to the $2\ 3S + 2\ 3P$ interaction. Transitions involving higher lying states will, of course, occur at shorter wavelengths.

The spectroscopy of the $2,1 \ ^3\Sigma_u^+$ state raises a different set of issues. There may be observed a wealth of absorptions at wavelengths $\lambda < 1080$ nm which correspond to transitions involving the rich manifold of $^3\Sigma_g^+$ and $^3\Pi_g$ states which themselves correspond to asymptotes lying above $2 \ ^3S + 2 \ ^3S$.⁸ If the $2,1 \ ^3\Sigma_u^+$ state has a sufficiently small autoionization cross section one could observe optically allowed transitions at $\lambda < 95$ nm which correspond to emissions to $1,n \ ^3\Sigma_g^+$ and $1,m \ ^3\Pi_g$ states in the singly excited manifold.

Table 5. Vibrational Energy Levels for the $2,1 \ ^5\Sigma_g^+$ and $2,1 \ ^3\Sigma_u^+$ States of He_2

v	$2,1 \ ^5\Sigma_g^+$ G (v) (cm^{-1})	v	$2,1 \ ^3\Sigma_u^+$ G (v) (cm^{-1})
0	71.37	0	153.61
1	204.68	1	453.86
2	325.19	2	741.95
3	433.06	3	1016.74
4	528.21	4	1278.77
5	610.80	5	1527.38
6	681.38	6	1761.83
7	740.08	7	1981.93
8	786.92	8	2187.59
9	822.64	9	2378.21
10	848.32	10	2553.47
11	862.97	11	2713.12
12	869.49	12	2856.81
13	873.77	13	2984.01
14	877.37	14	3094.31
15	880.48	15	3187.90
16	883.19	16	3265.65
		17	3328.09
		18	3375.22
		19	3406.22

V. CONCLUSION

Potential curves for the $2,1 \ ^5\Sigma_g^+$ and $2,1 \ ^3\Sigma_u^+$ states of He_2 which correspond to the $2 \ ^3S + 2 \ ^3S$ asymptote are calculated at the second order CI level where the excitations were taken from a small multireference base. The rich set of specially optimized basis functions used in these calculations suggest that these potential curves are the most reliable currently available for these states.

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APPENDIX

A NOTE ON NOTATION

APPENDIX A. A NOTE ON NOTATION

In dealing with highly excited states of alkali diatomic molecules, one of us (DDK) has found it to be much more convenient to number the states of a given symmetry from the (energetically) lowest lying to the highest rather than to use the more conventional letter designation. In the present studies of highly excited states of He_2 , we are dealing with states corresponding to two different ionization manifolds but of the same symmetry.

We use a two-index scheme to denote the relative energy ordering of the molecular states asymptotically. The first index denotes the ionization manifold and the second index indicates the energy rank of the state in question among all states of identical symmetry which belong to the same ionization manifold. For example, any state of He_2 which corresponds asymptotically to an energy which lies below that of $\text{He}(1s^2) + \text{He}^+(1s)$ would carry a first index of 1 (to signify the first ionization manifold or a singly excited state). Any state which corresponds asymptotically to an energy between that of a pair of $\text{He}(1s2s\ ^3S)$ atoms and a pair of $\text{He}^+(1s)$ ions carries a first index of 2 (to indicate a doubly excited state or, equivalently, a member of the second ionization manifold). The extension to higher lying states in the third and fourth ionization manifolds of He_2 is obvious.

The use of the second index which ranks states by energy is self-evident. There is no problem with states which are degenerate asymptotically since the molecule will eventually break the degeneracy as smaller separations are approached.

In this paper we discuss the following states of He_2 : $2,1\ ^5\Sigma_g^+$, $2,1\ ^3\Sigma_u^+$, $2,1\ ^1\Sigma_g^+$, $1,1\ ^3\Sigma_u^+$, $1,\infty\ ^1\Sigma_g^+$, for example. Clearly the first three states are the lowest lying states of their symmetry within the second ionization manifold; the $1,1\ ^3\Sigma_u^+$ state is the lowest of its symmetry within the first ionization manifold; the highest lying state of $^1\Sigma_g^+$ symmetry within the first ionization manifold is denoted by $1,\infty\ ^1\Sigma_g^+$.

For states which lie within the first manifold we recommend eliminating the first index where it is understood to be 1. Thus, our suggested notation is consistent with that which Konowalow and Fish¹³ introduced a few years ago to describe excited states of the first ionization manifold of Li_2 , and which has been used by a number of authors subsequently.

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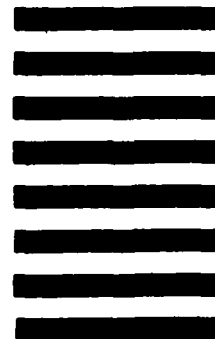


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